

**Originator: Kenyon C. Carlson, Manager  
ADEQ QA Unit**

**Contact For  
Information: Kenyon C. Carlson, Manager  
ADEQ QA Unit**

## **METHODS 200.7; 200.8; & 200.9**

### **I. SCOPE AND APPLICATION:**

Metals may be determined by atomic absorption (AA), inductively coupled plasma (ICP), or, with somewhat less precision and sensitivity by colorimetric methods. The absorption methods include flame and electrothermal techniques (graphite furnace atomic absorption). Flame methods are generally applicable at moderate concentration levels in both clean and complex matrix systems. Electrothermal methods (GFAA) can generally increase sensitivity if the matrix affects are not severe. Matrix modifiers frequently can compensate for many types of matrix effects. ICP techniques are applicable over a broad linear range and are particularly sensitive for refractory elements. The detection limits for ICP methods are higher than for those for electrothermal methods. Colorimetric methods are applicable when interferences are known to exist within a particular method.

This is a general purpose procedure for the collection of water samples for the analysis of metals and trace elements in ground waters, surface waters, and drinking water supplies. This method is applicable to the following analytes:

<b><u>Analyte</u></b>		<b><u>Chemical Abstract Services Registry Numbers (CASRN)</u></b>
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4

<u>Analyte</u>		<u>Chemical Abstract Services Registry Numbers (CASRN)</u>
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Phosphorous	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica	(SiO <sub>2</sub> )	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Vanadium	(Zn)	7440-66-6

## II. REAGENTS:

- Nitric acid (ultra high purity grade) 1:1 dilution. Add 500 ml of concentrated ultra pure nitric acid to 400 ml of ASTM type I water (reagent water-- free of analytes) and dilute to a volume of 1 liter.

## III. MATERIALS:

- 1 liter (32 oz) high density polyethylene bottles with poly-foam lined screw on caps.
- pH indicator paper (low end)
- Latex gloves
- Paper towels & Kim Wipe napkins
- Plastic container for disposal of used pipette tips
- Disposable glass pipettes and rubber bulb.
- Protective eyewear

#### IV. PROCEDURE:

1. Remove any attachments such as hoses, screens or aeration devices on the faucet. Inspect the faucet for anything that may fall into the sample container.
2. Open the tap and allow the system to flush for approximately 10 minutes. This should be sufficiently long enough to get a representative sample.
3. Remove the cap from the polyethylene container. Do not rinse the container as it has already been acid rinsed and may already contain acid as a preservative.
4. To fill, tip the bottle at about a 45° angle into the stream of water. Slow the stream sufficiently so as to be able to anticipate when the bottle is nearly full and thus avoid over flowing. Fill the bottle to the fill line or within ½ inch of the top. This will allow enough space for mixing and the addition of any additional acid if required.
5. Remove the bottle from the flow and recap. Invert the container five times.
6. Place a pH indicator test strip on a dry opened paper towel. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Moisten the pH indicator test strip with the aliquot from the glass pipette and immediately flick the pH indicator test strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference pH range. A determination must be made within 30 seconds.
7. If the pH is  $\leq 2$ , recap the bottle firmly, dry the sample bottle, attach the sample/laboratory label to the bottle and secure the chain of custody seal around the cap. Record the results in field notebook and place the sample bottle in the ice chest.
8. If the pH is not  $\leq 2$ , add 3 ml of 1:1 nitric acid ( $\text{HNO}_3$ ), recap the bottle firmly and invert the bottle 5 times.
9. Place a pH indicator test strip on a dry opened paper towel. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Moisten the pH indicator test strip with the aliquot from the glass pipette and immediately flick the pH indicator test strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference pH range. A determination must be made within 30 seconds.
10. If the pH is  $\leq 2$ , recap the bottle firmly, dry the sample bottle, attach the sample/laboratory label to the bottle and secure the chain of custody seal around the cap. Record the results in field notebook and place the sample bottle in the ice chest to cool to 4°C.

#### **IV. PROCEDURE (continued):**

11. Continue the process of adding acid to the sample, recapping, mixing, and testing until the pH of the sample reaches a pH of  $\leq 2$ . Remember to note the amount of acid added to the water sample in the field notebook.

#### **V. SAMPLE TRANSPORT:**

After obtaining the water samples (in duplicate if necessary), attach the preprinted sample label onto the bottle(s) as well as the completed chain of custody seal around the plastic cap of each sample bottle. Place the sample bottle(s) into the ice chest for transport. The samples must be chilled and preserved at a temperature of 4°C and maintained at that temperature until analysis. Always use chopped, grated, or dry ice when chilling the samples for transportation. Never use “blue ice” as the samples may not chill adequately.

Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be at 4°C upon arrival at the laboratory. Samples that cannot be acid preserved at the time of collection because of sampling limitations or transport restrictions should be acidified with nitric acid (HNO<sub>3</sub>) to a pH < 2 upon receipt in the laboratory and allowed to sit approximately sixteen hours. This waiting period is to allow any inorganic metals to return back into solution in the event they may have precipitated or “plated out” along the inside of the sample container as a result of inadequate acidification at the time of collection.

#### **VI. SAMPLE STORAGE:**

Store samples at 4°C until digested for analysis.

#### **VII. DEFINITIONS:**

- A. *Aliquot*: A measured portion of a sample taken for analysis.
- B. *Flame atomic absorption*: A portion of the digested sample is directly introduced into a flame. The sample is atomized in the flame while the light from a hollow cathode ray lamp is directed through it. Some of the light is absorbed by the element in the sample and that amount of absorbance is used to calculate the concentration of the element in the original sample.
- C. *Graphite furnace atomic absorption*: A small amount of digested sample is placed in a graphite tube where it is dried and heated to very high temperatures. Upon heating, the sample is atomized in the source light path where absorption takes place.

## VII. DEFINITIONS (continued):

- D. *Quantitative* results are obtained by comparing sample absorbances to that of analytical standards analyzed in the same way
- E. *Inductively coupled plasma*: Unlike the AA procedures, ICP utilizes atomic emission to quantitate various elements. Just as with AA where each element has its own characteristic atomic “absorption spectrum”, each element undergoing ICP analysis has its own characteristic atomic “emission spectrum” and a unique set of wavelengths that it emits at very high temperatures. This is achieved by heating the sample using plasma, to high temperatures (e.g., 10,000° Kelvin), at which point the characteristic wavelengths are emitted. The plasma is a flame-like system of ionized, very hot gas (typically argon), which provides a nearly ideal emission source. The emitted light is detected by a diode array detector and measured. The intensity of any particular emitted wavelength depends on the concentration of atoms of that element present in the sample.
- F. *Matrix effects*: The influence of the sample matrix or sample components upon the ability of analytical methods to qualitatively identify and quantitatively measure target compounds in environmental samples.

## VIII. SAFETY:

The use of protective eyewear and laboratory quality latex gloves is highly recommended when collecting and preserving samples.

## IX. SUMMARY OF METHOD:

METHOD 200.7--(ICP analysis) This method describes a technique for simultaneous or sequential multi element determination of metals and trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectrometric technique. Samples are nebulized and the aerosol that is produced is directed to the plasma torch where desolvation and excitation occur. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer, and line intensities are monitored by a photosensitive device (e.g. photomultiplier tube or diode array). Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for the variable background contribution in the determination of the analytes.

## IX. SUMMARY OF METHOD (continued):

METHOD 200.8--(ICP-MS analysis) This method is identical to 200.7 up to the transfer of nebulized sample to the plasma torch resulting in atomization and ionization. However, the ions in this analytical method are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 atomic mass unit (amu) peak at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier or Faraday detector and the ion information is processed by the data handling system. Instrumental drift, as well as suppressions or enhancements of instrument response caused by the sample matrix, must be corrected by the use of internal standardization.

METHOD 200.9--(GFAA analysis) This method describes the determination of the metals listed in the beginning of the SOP using graphite furnace atomic absorption (GFAA). In GFAA, the sample (and matrix modifier, if required) is first pipetted onto the platform or a device which provides delayed atomization. The sample is then dried at a relatively low temperature (~120°C) to avoid spattering. Once dried, the sample is normally pretreated in a char or ashing step which is designed to minimize the interference effects caused by the concomitant sample matrix. After the char step, the furnace is allowed to cool prior to atomization. The atomization step is characterized by the rapid heating of the furnace to a temperature where the metal (analyte) is atomized from the pyrolytic graphite surface. The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp or an electrodeless discharge lamp. Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, an instrumental background correction device is necessary to subtract from the total signal the component which is nonspecific to the analyte. Instrumental drift, as well as suppressions or enhancements of instrument response caused by the sample matrix, must be corrected for by the method of standard addition.